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(54) Title: MACHINE DISHWASHING AND RINSE AID COMPOSITIONS

(57) Abstract

Use is provided of a low-MW (1000-60,000) block copolymer comprising 20-95 mole % of itaconic acid units and 5-80 mole % of vinyl alcohol or vinyl acetate units, as an antiscalant in machine dishwashing operations. The polymer is biodegradable and can be incorporated as ingredient in the main wash machine dishwashing compositions or in rinse aid compositions.

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MACHINE DISHWASHING AND RINSE AID COMPOSITIONSField of the invention

This invention relates to machine dishwashing and
5 warewashing compositions. These compositions are used for
the cleaning of house and kitchenwares, such as pots, pans,
dishes, cups, saucers, bottles, glassware, crockery,
cutlery and other kitchen utensils in automatic dishwashing
and warewashing machines. For brevity's sake, these
10 compositions are referred to hereinafter as machine
dishwashing compositions. The invention also relates to
rinse aid compositions for use in the final rinse step of
the washing machine operation.

15 Background of the invention

Machine dishwashing compositions usually contain, as main
components, a builder or builder mixture, buffering and/or
alkaline agents, and optionally a surfactant, a bleaching
agent which may be a chlorine or oxygen bleach, and lately
20 often also enzymes (e.g. protease, amylase, cellulase,
lipases and mixtures thereof). Rinse aid compositions
usually comprise an aqueous liquid containing, as major
components, a low-foaming nonionic surfactant and an
organic chelating agent, e.g. citric acid.

25

It is known that high concentrations of carbonic species
during the main wash cycle and final rinse in a dishwasher
can lead to the formation of calcium carbonate deposits
(scaling) on the washed articles, visible particularly on
30 glasses as white deposit, and also on machine parts,
especially the heater elements. Tap water of a relatively
high water hardness and insufficient softening in the
machine increase the problem dramatically. Other parameters
involved in the scaling process are temperature (high
35 temperature increases deposition) and pH (higher pH appears
to increase scaling). This phenomenon can occur with any
machine dishwashing product formulation, although to a much

lesser extent with conventional products based on the highly effective sodium triphosphate builder. In the last few years, however, machine dishwashing product manufacturers have gradually changed over to low-phosphate, 5 non-phosphate and even zero-P product formulations. These products have currently become an important part of machine dishwashing products on the market. Because non-phosphate and zero-P formulations inherently contain less effective builders as phosphate replacements, e.g. citrates, 10 carbonates, zeolites, which also have inadequate scale-inhibiting properties, the risk of scaling with these products is higher than with the conventional sodium triphosphate products.

15 Scale formation on dishes and machine parts is thus an important problem that needs to be resolved or at least mitigated in formulating a machine dishwashing product, especially in the case of low-phosphate (e.g. less than the equivalent of 20% by weight, particularly 10% by weight of 20 sodium triphosphate) and phosphate-free machine dishwashing compositions, particularly zero-P machine dishwashing compositions.

In order to reduce this problem, co-builders, such as 25 polyacrylic acids or polyacrylates (PAA), maleic anhydride/(meth)acrylic acid copolymers, e.g. Sokalan CP5® ex BASF; and the various organic polyphosphonates, e.g. of the Dequest® range, have been added to phosphate-free machine dishwashing compositions. A drawback of these 30 polymers is that they are not sufficiently biodegradable and therefore environmentally less acceptable. The polyphosphonates, whilst being effective, are less acceptable as being P-containing products. It has furthermore been observed that, especially when phosphate-free machine dishwashing compositions containing such co-builders are used as main wash product in machine dishwashing operations, the visual appearance of articles, 35

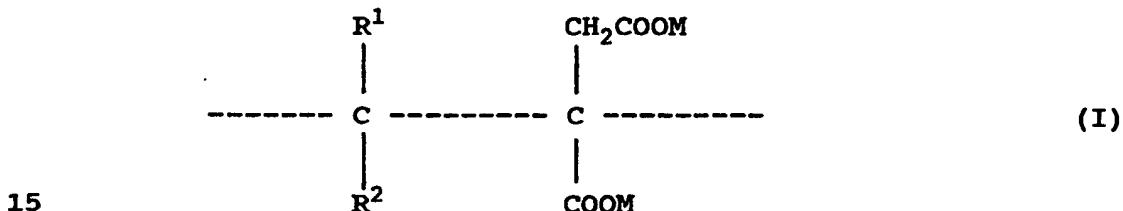
especially glasses, often deteriorates after a plurality of washings, despite the use of rinse aids.

Summary of the invention

5 It has now been found that a block copolymer having a weight average molecular weight ranging from 1000 to 60,000 and comprising:

(i) from 20 to 95 mole % of monomer units of the formula I:

10

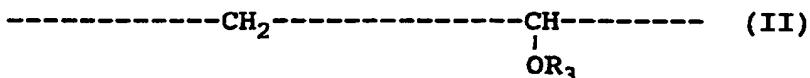


15

wherein each of R^1 and R^2 , which may be the same or different, represents a hydrogen atom, or a $\text{C}_1\text{-C}_{18}$ alkyl group; and M is a hydrogen atom, a solubilising cation or a 20 $\text{C}_1\text{-C}_{18}$ alkyl group; and

(ii) from 5 to 80 mole % of monomer units of the formula II:

25



OR_3

wherein R_3 represents a hydrogen atom or the group $-\text{COR}^4$, wherein R^4 is a $\text{C}_1\text{-C}_{17}$ alkyl group, can be used as an effective anti-scaling agent in machine dishwashing compositions and/or in rinse aid compositions to inhibit 30 calcium carbonate scale formation on washed articles and machine parts without the drawbacks of anti-scalants of the art.

The copolymers usable in this invention are non-phosphorus-containing compounds and are fully biodegradable. They have a weight average molecular weight preferably ranging from 35 1500 to 50,000, and more preferably from 2000 to 40,000.

Detailed description of the invention

Accordingly, the invention provides the novel use of a block copolymer as hereinbefore defined (further also referred to as "ITA/VA") as an anti-scaling agent in 5 machine dishwashing compositions and/or in rinse aid compositions.

The invention also provides a method for inhibiting calcium carbonate scale formation during a warewashing process by 10 applying a machine dishwashing composition and/or rinse aid composition including the above-defined block copolymer as an anti-scaling agent.

Detailed Description of the Invention

15

The Copolymer

The ITA/VA block copolymer is characterised by the presence of monomeric units (i) derived from itaconic acid or a homologue thereof, in acid or salt form, and monomer units 20 (ii) derived from vinyl alcohol or esters thereof.

The copolymer comprises from 20 to 95 mole % of units (i) and from 5 to 80 mole % of units (ii). Preferably, the copolymer comprises from 20 to 80 mole % of units (i) and 25 from 20 to 80 mole % of units (ii).

The weight average molecular weight ranges from 1000 to not more than 60,000. Copolymers of molecular weight higher than 60,000 are excellent builders, but ineffective as 30 anti-scalants. Preferred copolymers are therefore those having weight average molecular weight of not more than 50,000, more preferably not more than 40,000. Preferred weight average molecular weight (Mw) ranges are from 1500 to 50,000, particularly from 2000 to 40,000.

35

Within these ranges, it applies as a rule that the higher the molecular weight, the higher a mole % of units (ii) is

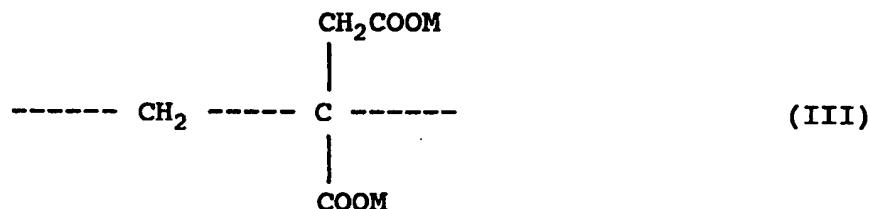
required.

In the formula (I) above, M is preferably a hydrogen or a sodium, potassium, ammonium or lower alkyl-substituted 5 ammonium ion, and most preferably a sodium ion.

In preferred units (i), both R¹ and R² represent a hydrogen atom, i.e. the units are of the formula III and are derived from itaconic acid itself or a salt thereof:

10

15



The units (ii) are derived from vinyl acetate. In the polymer, they may be present in the ester form as vinyl 20 acetate units, or in hydrolysed form as vinyl alcohol units.

Examples of preferred copolymers are copolymers of itaconic acid and vinyl acetate of the following compositions and Molecular Weights (Mw).

25

30

35

<u>ITA/VA mole ratio</u>	<u>Mw</u>
20/80	29,000
50/50	5,300
70/30	20,500

The copolymer may also be a terpolymer of monomer units (i) and (ii), such as, for example, a terpolymer containing vinyl acetate (48 mole %), disodium itaconate (48 mole %), and mono-lauryl itaconate (4 mole %), having Mw 15,200.

Preparation of the copolymers

The polymers may be prepared by copolymerising from 20 to 95 mole % of a compound of the formula IV, that is to say, itaconic acid or ester or an alkyl substitution product 5 thereof in acid or salt form,



15 with 5 to 80 mole % of vinyl acetate. Optionally, the acetate groups may subsequently be hydrolysed but that does not appear to be essential.

20 The polymerisation may conveniently be carried out in aqueous or aqueous/organic solution. The preferred media are water and water/ethanol. Polymers have also been prepared successfully in dilute hydrochloric acid.

25 The copolymerisation is advantageously conducted in the presence of a water-soluble initiator. The use of a water-soluble redox initiator is especially preferred.

30 Examples of suitable initiators include sodium, potassium or ammonium persulphate, 2,2'-azobis(amidinopropane) hydrochloride, 2,2'-azobis(cyanopentanoic acid); and redox initiators, such as hydrogen peroxide (Fenton's reagent) and other hydroperoxide systems. A preferred redox initiator is sodium or potassium persulphate in combination with sodium or potassium bisulphite.

35 The polymerisation may typically be performed under a nitrogen atmosphere in a degassed solvent at ambient pressure, or in a sealed tube under vacuum. The entire monomer charge may be polymerised in a single batch, or

alternatively the vinyl acetate may be fed in incrementally as the polymerisation progresses, the latter method being preferred. The polymerisation reaction proceeds steadily at temperatures of 40-100°C; redox initiators are generally used at relatively low temperatures, in the region of 40°C, while other initiators may require temperatures in the 50-100°C range. For a reasonable conversion, a reaction time of 1-5 days is required, typical yields being from 20 to 83%, depending on the reaction time.

10

Effectively, the level of the block copolymer ITA/VA to be included in the machine dishwashing composition or the rinse aid composition, or in both, may range from about 0.1 to about 15% by weight, preferably from 0.25% to about 10%, particularly from 0.5 to 10% by weight of the composition. Usually, an amount of not more than 5% by weight of the compositions will be sufficient.

The machine dishwashing composition of the invention will normally also contain a builder or builder mixture, buffering and/or alkaline agents, optionally but preferably also a bleaching agent and an enzyme or mixtures of enzymes.

25 The builder material

Builder materials (phosphates and non-phosphate builder materials) are well known in the art and many types of organic and inorganic compounds have been described in literature. They are normally used in all sorts of cleaning compositions to provide alkalinity and buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and/or remove alkaline earth metal ions from washing solutions.

35 The builder material usable herein can be any one or mixtures of the various phosphate and non-phosphate builder materials. The present invention, however, has particular

applicability to non-phosphate and zero-P compositions containing non-phosphate builder materials, such as, for example, the alkali metal citrates, carbonates and bicarbonates; nitrilotriacetic acid (NTA); dipicolinic acid 5 (DPA); oxydisuccinic acid (ODS); alkyl and alkenyl succinates (AKS); zeolites; layered silicas and mixtures thereof. They may be present in the composition of the invention in an amount of from 10% up to about 90% by weight, preferably from 20% to 80% by weight.

10

Particularly preferred builders are citrates, DPA, ODS, alkenyl succinates, carbonates, bicarbonates, and also the higher molecular weight block copolymers ITA/VA having M_w greater than 60,000.

15

Accordingly, in one specific embodiment the invention provides a machine dishwashing composition comprising, as builder, a block copolymer ITA/VA having $M_w > 60,000$ and, as anti-scalant, a block copolymer ITA/VA of $M_w < 60,000$ as 20 hereinbefore described.

The buffering and/or alkaline agent

This is normally an alkali metal silicate, preferably sodium silicate at a level of from about 1 to about 70% by 25 weight, preferably from 5 to 40% by weight. This material is employed as a cleaning ingredient, source of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. Especially effective is sodium silicate having a mole ratio of $SiO_2:Na_2O$ of from about 1.0 to about 3.3., 30 preferably from about 1.8 to about 2.2, normally referred to as sodium disilicate.

NaOH and/or KOH are also commonly used to provide alkalinity in compositions for industrial warewashing 35 machines.

The bleaching agent

If present, the amount of bleaching agent will preferably lie in a range from 1 to 30% by weight. Alkali metal hypochlorite may be incorporated. Other chlorine bleaches 5 are alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids.

Preferred bleaches are the peroxygen bleaches, such as sodium perborate (tetra- or monohydrate) or sodium 10 percarbonate. These are preferably used in conjunction with a bleach activator which allows the liberation of active oxygen species at a lower temperature. Numerous examples of activators of this type, often also referred to as bleach or peracid precursors, are known in the art. Preferred 15 bleach activators are tetraacetyl ethylene diamine (TAED), glucose pentaacetate (GPA) and the mono long-chain acyl tetraacetyl glucoses as disclosed in WO 91/10719, but other activators, such as choline sulphophenyl carbonate (CSPC), as disclosed in US Patents 4,751,015 and 4,818,426 can be 20 used. The amounts of sodium perborate or percarbonate and bleach activator in the compositions preferably do not exceed 20% and 10% by weight, respectively, e.g. from 4-20% and from 2-10% by weight, respectively.

25 Another peroxygen bleach is potassium monopersulphate. Further peroxygen bleaches which may be used are the organic peroxyacids and their metal salts. Typical peroxyacids include:

- (i) peroxybenzoic acid and ring-substituted
- 30 peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- (ii) aliphatic and substituted aliphatic monoperoxy acids, e.g. peroxylauric acid and peroxystearic acid;
- (iii) 1,12-diperoxydodecanedioic acid (DPDA);
- (iv) 1,9-diperoxyazelaic acid;
- 35 (v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vi) 2-decyldiperoxybutane-1,4-dioic acid; and

(vii) phthaloylamido peroxyacrylic acid (PAP).

Instead of, or together with, said bleach activators, a bleach catalyst, such as the manganese complexes of 5 EP-A-458,397 and the sulphonimines of US Patents 5,041,232 and 5,047,163 may also be added.

Enzymes

Amylolytic and/or proteolytic enzymes are normally used.

10 The amylolytic enzymes usable herein can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in GB Patent N° 1,296,839, cultivated from the strains of *Bacillus licheniformis* NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC 15 8480 and ATCC 9945 A. Examples of such amylolytic enzymes are those produced and distributed under the tradenames of SP-95® and Termamyl® by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 20 to 10 Maltose Units/milligram. They may be present in the composition of the invention in amounts such that the final composition has amylolytic enzyme activity of from 10^3 to 10^6 Maltose Units/kilogram.

25 The amylolytic activity as referred to herein can be determined by the method as described by P.Bernfeld in "Method of Enzymology", Volume I (1955), page 149.

30 The proteolytic enzymes usable herein are, for example, the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase®, supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, supplied by NOVO Industri A/S, Copenhagen, Denmark. Particularly suitable 35 are proteases obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available from NOVO Industri A/S under the

tradenames of Esperase® and Savinase®. The preparation of these and analogue enzymes is described in GB Patent N° 1,243,784. These enzymes are generally presented as granules, e.g. marumes, prills, T-granulates etc., and may 5 have enzyme activities of from 500 to 1700 Glycine Units/mg. The proteolytic enzyme activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology", Vol. 22 (1938), page 79 (one Anson unit/gram = 733 Glycine Units/milligram).

10 In the compositions of the invention, proteolytic enzymes may be present in amounts such that the final composition has proteolytic enzyme activity of from about 10^6 to 10^8 Glycine Units/kilogram.

15 Other enzymes, such as lipolytic enzymes, may also be incorporated to improve fat removal. Typical examples of commercial lipolytic enzymes are Lipase YL, Amano CE, Wallerstein AW, Lipase My, and Lipolase ex Novo Ind.

20 Other optional ingredients
Surfactants, though not strictly essential, may also be present for detergency, soil removal, foam depression and/or as rinse aids. If present, they can be used in an 25 amount of up to about 60% by weight, depending upon their types and properties. Normally, in a properly built or highly built composition as is conventional, only small amounts of low- to non-foaming nonionic surfactant, in the order of 0.1-5% by weight, are used, preferably from 0.1- 30 4%, to aid detergency and particularly to suppress excessive foaming caused by some protein soil. Higher amounts, i.e. 5-60% by weight of highly deteritive surfactants, such as the high HLB nonionic surfactants, the anionic sulphate or sulphonate surfactants and the alkyl 35 polyglycoside class of surfactants, may be used in lower builder-containing active/enzyme-based compositions. In the context of the present invention, a surfactant content from

0 to less than 5% by weight is preferred.

Other optional ingredients that can be further included in minor amounts are clay minerals, particularly the layered 5 clay minerals to reduce film and spot formation on washed articles. Typical and particularly preferred commercial clay products are the synthetic hectorites manufactured and supplied by Laporte Industries Ltd, England, as Laponite® clays, e.g. Laponite S, Laponite XLS, Laponite RD and 10 Laponite RDS.

Other materials usable herein for this purpose are hydrotalcite compounds, especially Zn/Al hydrotalcite, as described in Applicant's co-pending European Application N° 15 92307241.7.

Zinc salts, both soluble and insoluble zinc salts, can also be incorporated as adjuncts for minimizing glass corrosion.

20 An inert particulate filler, especially sodium sulphate, may also be incorporated, though in compact powdered composition it should desirably be omitted as practically possible.

25 The products of the present invention can be manufactured and presented in any physical form, such as a powder, liquid, paste or solid blocks or tablets, and are preferably formulated such that they provide a wash liquor with a pH of from 8-11, preferably from 9.0-10.5 (measured 30 at a concentration of from 0.1-0.3% by weight in water).

As explained, the invention is also applicable to conventional rinse aid compositions, which usually comprise an aqueous solution comprising a low-foaming nonionic 35 surfactant, citric acid or sodium citrate and optionally a hydrotrope, such as a lower alcohol or sodium xylene sulphonate.

The copolymer ITA/VA according to the invention may be added to the rinse water as such, or it may be added thereto in the form of a liquid solution in water, or in the form of a composition in any suitable physical form

5 comprising the polymer and other suitable or desirable ingredients as normally used in rinse aid products. Such other suitable ingredients may be low levels of wetting or detergent surfactants; organic acids such as citric acid; hydrotropes; alcohols; perfumes; germicides; anti-corrosion

10 agents; clays, particularly layered clay minerals, such as the Laponite® clays, supplied by Laporte Ind. Ltd etc. Suitable physical forms are powders, liquids, tablets, blocks, granulates etc. However, liquid is a suitable preferred form.

15

To be effective, the level of the polymer in the rinse liquor may vary, depending upon whether the main wash composition already contains the anti-scalant polymer or not. As a rule, the rinse liquor may contain the defined

20 polymer in concentrations of from 0.2 ppm to about 30 ppm, preferably from 0.5 ppm to 20 ppm, with about 1-10 ppm being the optimum. These correspond to a level of about 0.1% to about 15%, preferably from 0.25% to 10%, and from 0.5-5% by weight as optimum in rinse aid compositions

25 normally used at a dosage level of about 1-3 ml/6 litre rinse water.

Accordingly, in one more aspect the invention provides a process for warewashing in a dishwashing machine comprising

30 washing the articles in a main wash cycle and rinsing them in a rinse cycle, characterised in that in the rinse step there is added to the rinse water a copolymer ITA/VA as hereinbefore defined in an amount such that the rinse liquor contains the defined polymer in a concentration of

35 from 1 ppm to about 20 ppm, preferably from 5 ppm to 15 ppm.

The invention will now be further illustrated by way of the following non-limiting Examples.

Characterisation of the polymers

- 5 The polymers were characterised by infra-red spectrometry and in some cases by nuclear magnetic resonance spectroscopy.
- 10 The infra-red instrumentation used included the Nicolet (trademark) 1705X Fourier Transform infra-red spectrometer with MCT detector using the Nicolet 1280 processor, and the Nicolet SDXC Fourier Transform infra-red spectrometer with DGS detector using the Nicolet 62 processor.
- 15 ^1H and ^{13}C NMR spectra were run on a Brucker (trademark) WM 360 MHz Fourier Transform spectrometer.

- 20 Number-average and weight-average molecular weights of polymeric materials were determined by gel permeation chromatography. This was carried out, using a Hewlett Packard (trademark) HP 1090 liquid chromatography fitted with a 30 cm x 7.5 cm TSK gel linear GMPW column. Organic solvent-soluble polymers were measured against polystyrene standards, and water-soluble polymers against polyethylene glycol.

Biodegradability

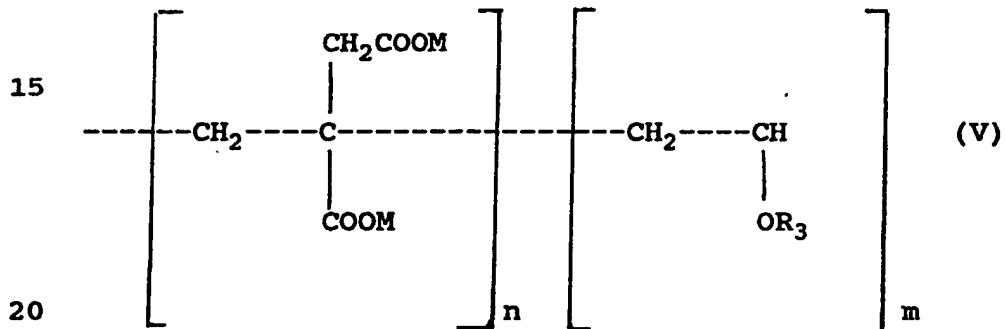
This was investigated by means of the following tests as described in the OECD Guidelines.

- 30 (a) Modified SCAS test as described in OECD Guideline 302a. This test measures removal of test material by dissolved organic carbon analysis. It is believed that an 80% removal is a reasonable indication of biodegradability
- 35 or adsorption.

(b) Modified Sturm test as described in OECD Guideline 302b. This test measures CO_2 production from the test material under standard condition. A 60% conversion to CO_2 in the Sturm test is an indication of ready 5 biodegradability.

Examples I and II
This Example describes the preparation of two copolymers of differing molecular weights, each from 50 mole % vinyl acetate and 50 mole % itaconic acid. 10

These polymers have the formula V:



wherein R_3 indicates hydrogen (predominant) or an acetyl group, and the indices n and m indicate the numbers of repeating units.

25

Preparation of the copolymer of Example I
Vinyl acetate (23.4 ml, 0.25 mole), itaconic acid (30 g, 0.25 mole) and degassed water (200 ml) were charged into a flange flask and stirred at 40°C under a nitrogen atmosphere. The redox initiator, comprising sodium persulphate (0.8 g) and sodium metabisulphite (0.4 g), was added in increments, each of 0.3 g, over four days. The polymer-containing solution was concentrated to approximately half volume using a rotary evaporator and the 30 concentrate poured into acetone. This precipitated the polymer which was washed with portions of acetone. The 35 copolymer was then vacuum-dried.

The copolymer was then neutralised and hydrolysed with sodium hydroxide (5.4 g, 1.35 mol) in hot water (50 ml). The sodium salt of the hydrolysed copolymer was precipitated into a large excess of ethanol (300 ml). After 5 separation and removal of ethanol, the copolymer was dissolved in water, and freeze-dried. The yield was 17.3 g (32%).

Preparation of the copolymer of Example II

10 The copolymer of Example II was prepared by a similar method, but using sodium persulphate alone as the initiator. The reaction temperature was 60°C. The yield was 25.8 g (48%).

15 Characterisation

(i) Fourier transform infrared spectrum (KBr wafer)
Short-chain polycarboxylate (C=O stretch) 1580 cm^{-1}

20 (ii) ^1H NMR (deuterium oxide)

Chemical shifts (ppm):

σ 1.6 – 3.3 backbone protons (CH_2 and CH)

(iii) Aqueous GPC molecular weights

25

	M_n	M_w	D
Example I	18,000	31,500	1.7
Example II	20,000	34,900	1.7

30 (iv) Biodegradation

The SCAS test for the polymer of Example I showed 93.3% removal, indicating virtually complete biodegradation.

Example III

35 Preparation of Copolymer (III) ITA/VA (50/50) and M_w 5300

Itaconic acid (22.7 g, 0.174 mol) and vinyl acetate (15.0 g, 0.174 mol) were stirred with degassed 0.5 M

hydrochloric acid (80 ml) at 40°C. Sodium persulphate (0.5 g) was added in four portions over a period of 48 hours. The resulting copolymer was isolated by precipitation into acetone. It was then purified further by 5 two more precipitations into acetone from concentrated aqueous solutions.

To obtain the sodium salt, the copolymer was then dissolved in water, neutralised with 6% sodium hydroxide solution to 10 pH 8.5 and then freeze-dried. The yield was 44%.

Polymer characterisation

(ITA) : (VA)	Mn	Mw	D
50 : 50	3000	5300	1.8

15

Example IV

Preparation of copolymer (IV) - ITA/VA (70/30) and Mw 20,500

20 This copolymer was prepared using the same method as described in Examples I and II.

Polymer characterisation

(ITA) : (VA)	Mn	Mw	D
70 : 30	8600	20,500	2.4

Example V

Preparation of Copolymer (V) - ITA/VA (20/80) and Mw 29,000

30 Sodium dodecyl sulphate (0.2 g.) and itaconic acid (9.1 g, 0.07 mol) were dissolved in water (240 ml) and the solution was degassed at 60°C. Vinyl acetate (24.1 g, 0.28 mol) was then added and the mixture stirred. After 30 minutes, 0.2 g of sodium persulphate initiator in water (4 ml) was added 35 and polymerisation was left for 6 hours. Another 0.3 g of the initiator in water (6 ml) was added incrementally over a period of 72 hours.

The polymerisation liquor was concentrated to dryness using a rotary evaporator. The solid obtained was dissolved in acetone and the copolymer precipitated into diethyl ether. The process was repeated twice, giving a white material.

5 The copolymer was vacuum-dried at 30°C. Yield 12.9 g (39%).

To obtain the sodium salt, the copolymer was dissolved in water (200 ml), neutralised with sodium hydroxide at room temperature to pH 8.5 and then freeze-dried. Yield 11.3 g
10 (31%).

Polymer characterisation

(ITA) : (VA)	Mn	Mw	D
20 : 80	8,200	29,000	3.55

15

Examples VI-VII

Set-up scaling experiments.

20 The build-up of scale (calcium carbonate) on dishes in a machine dishwashing process was investigated in small-scale model scaling experiments. The wash cycles in such experiments are simulated by heating a washing solution containing pre-weighed glass slides. The weight increase of
25 these slides during a 9-cycle build-up experiment is considered to be due to the deposition scale. A combined main wash and final rinse experiment was used to study scale protection with a main wash composition.

30 Main wash/final rinse experiment

In a 3-litre beaker glass, 2.7 gram of a composition is added to 1.5 litre of hard water. This water is made by adding calcium chloride, magnesium chloride and sodium bicarbonate to demineralised water, in such amounts that a
35 total water hardness of 40 degrees French¹ (molar ratio Ca/Mg:4/1) and a temporary (bicarbonate) hardness of 32 degrees French² is obtained. After placing pre-weighed

glass slides (5x5x0.1 cm) in this solution, the temperature is raised from 20 to 65°C at a rate of 2.5°C per minute, and kept constant at 65°C for 12 minutes. This temperature profile simulates a main wash cycle and is obtained, using 5 a submerged electrical heating element and a programmable temperature controller. At the end of this cycle, the slides are taken out of the solution. One slide is used for the determination of the scale formation during this cycle and is replaced by a new slide. Subsequently, a final rinse 10 cycle is simulated by adding the remaining slides to 1.5 litre of water of the same hardness. At the same time, 1.5 ml of the main wash solution (simulating a 1/1000 carry-over from the main wash) is added. This final rinse solution is then heated from 20 to 70°C (2.5°C/min) and 15 kept isothermal for 10 minutes. At the end of this cycle, again one slide is removed for analysis and replaced by a new one. Generally, this procedure is repeated nine times.

1) 1°FH (Ca and/or Mg) is equivalent to 0.1 mmol/l CaCO_3 .
20 2) 1°FH (HCO_3^-) is equivalent to 0.2 mmol/l NaHCO_3 .

Main wash base composition (parts by weight)

sodium citrate	43.0
sodium disilicate	34.0
25 sodium perborate monohydrate	6.8
TAED	4.2
Laponite® clay	1.7
Nonionic surfactant	1.7

30

The Experiments were carried out with:

(A) The above main wash base composition.
35 (B) The above base composition + 2.5% CP5*
(C) The above base composition + 2.5% ITA/VA 50/50 copolymer of Mw 62,500.

(D) The above base composition + 2.5% ITA/VA 80/20 copolymer of Mw 81,800.

(VI) The above base composition + 2.5% ITA/VA 20/80 copolymer of Mw 29,000.

5 (VII) The above base composition + 2.5% ITA/VA 50/50 copolymer of Mw 5300.

(VIII) The above base composition + 2.5% ITA/VA 70/30 copolymers of Mw 20,500.

* maleic anhydride/acrylic acid copolymer ex BASF

10

The results are shown in the following Table 1.

Table 1

15 Scale build-up on glasses after 9 wash cycli

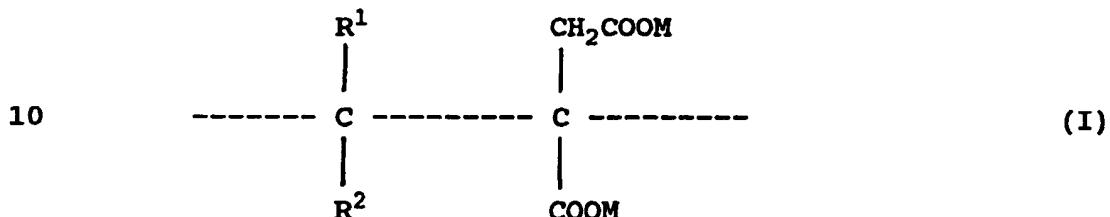
	<u>Composition</u>	<u>Weight increase (mg/slide)</u>
	A	45
	B	~ 2
20	C	26
	D	35
	VI	~ 2
	VII	~ 2
	VIII	~ 2

25

CLAIMS

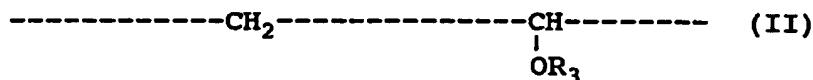
1. Use of a block copolymer having a weight average molecular weight ranging from 1000 to 60,000 and
 5 comprising:

(i) from 20 to 95 mole % of monomer units of the formula I:



wherein each of R¹ and R², which may be the same or
 15 different, represents a hydrogen atom, or a C₁-C₁₈ alkyl group; and M is a hydrogen atom, a solubilising cation or a C₁-C₁₈ alkyl group; and

(ii) from 5 to 80 mole % of monomer units of the formula
 20 II:



wherein R₃ represents a hydrogen atom or the group -COR⁴,
 25 wherein R⁴ is a C₁-C₁₇ alkyl group, as an anti-scaling agent in a machine dishwashing composition and/or rinse aid composition for inhibiting calcium carbonate scale formation on washed articles and machine parts.

30 2. Use according to Claim 1, wherein the block copolymer has a weight average molecular weight ranging from 1500 to 50,000.

3. Use according to Claim 1 or 2, wherein the block copolymer comprises from 20 to 80 mole % of monomer units of formula I and from 20 to 80 mole % of monomer units of formula II.

4. Use according to any of Claims 1-3, wherein R₁ and R₂ in the monomer units of formula I represent a hydrogen atom.

5 5. Use according to any of Claims 1-4, wherein M in the monomer units of formula I is selected from the group consisting of a hydrogen, potassium, sodium, ammonium, and a lower alkyl-substituted ammonium ion.

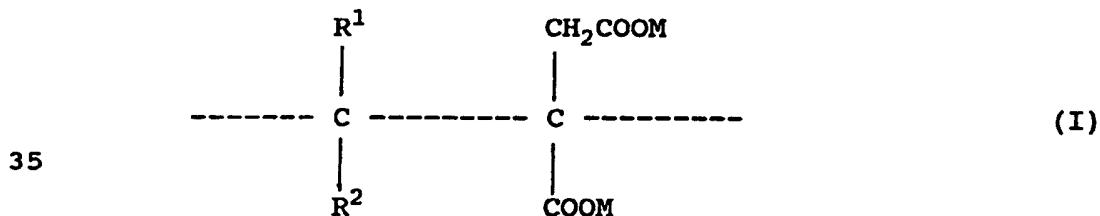
10 6. Use according to Claim 1, wherein M is a sodium ion.

7. Use according to any of Claims 1-6, wherein the machine dishwashing composition or rinse aid composition is formulated such that it provides a wash liquor with a pH of 15 from 8-11 (measured at a concentration of from 0.1-0.3% by weight in water).

8. Use according to any of Claims 1-7, wherein the level of the block copolymer in the machine dishwashing 20 composition and/or the rinse aid composition ranges from about 0.1 to about 15% by weight.

9. Method for inhibiting calcium carbonate scale formation during a warewashing process by applying a 25 machine dishwashing composition or rinse aid composition, including a block copolymer having a weight average molecular weight ranging from 1000 to 60,000, and comprising :

30 (i) from 20 to 95 mole % of monomer units of the formula I:

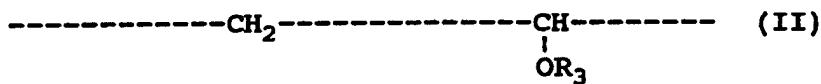


wherein each of R¹ and R², which may be the same or different, represents a hydrogen atom, or a C₁-C₁₈ alkyl group; and M is a hydrogen atom, a solubilising cation or a C₁-C₁₈ alkyl group; and

5

(ii) from 5 to 80 mole % of monomer units of the formula II:

10



wherein R₃ represents a hydrogen atom or the group -COR⁴, wherein R⁴ is a C₁-C₁₇ alkyl group, as an anti-scaling agent.

15

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/00026

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 054 548 (KURITA WATER INDUSTRIES) 18 February 1981 see page 1, line 32 - line 62; claims 1-3; example 12 -----	1-4,9
A	EP,A,0 425 068 (AUSIDET S.R.L) 2 May 1991 see page 1, line 17 - page 2, line 5 -----	1

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/00026

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